



HAL
open science

The mechanism of solution of aluminum oxide in MgSiO₃ perovskite

Jonathan F. Stebbins, Scott Kroeker, Denis Andrault

► **To cite this version:**

Jonathan F. Stebbins, Scott Kroeker, Denis Andrault. The mechanism of solution of aluminum oxide in MgSiO₃ perovskite. *Geophysical Research Letters*, 2001, 28, pp.615-618. 10.1029/2000GL012279 . insu-03597766

HAL Id: insu-03597766

<https://hal-insu.archives-ouvertes.fr/insu-03597766>

Submitted on 4 Mar 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Copyright

The mechanism of solution of aluminum oxide in MgSiO₃ perovskite

Jonathan F. Stebbins, Scott Kroeker

Dept. of Geological and Environmental Sciences, Stanford University, Stanford, California

Denis Andrault

Laboratoire des Géomatériaux, IGP, Paris, France

Abstract. We report ²⁷Al and ²⁹Si Nuclear Magnetic Resonance (NMR) spectra, collected at magnetic fields of 14.1 and 18.8 Tesla on samples as small as 1 mg, for Al-bearing MgSiO₃ perovskite synthesized at 26-28 GPa. For Al, we find a 1:1 ratio of two types of sites: a symmetrical, octahedral site and a low symmetry, distorted site that is most likely to be Al in modifications of normally eight-coordinated Mg sites. A charge coupled substitution of 2 Al for one Si and one Mg cation is strongly supported as the predominant mechanism in this pressure range.

Introduction

The most abundant mineral in the earth's lower mantle is thought to be MgSiO₃ with the perovskite structure [Knittle and Jeanloz, 1987; Zhang and Weidner, 1999]. After ferrous and/or ferric iron, the most important cation in solid solution in this phase is Al³⁺. The structure is composed of corner-shared octahedra (nominally occupied by Si⁴⁺) surrounding a larger, eight-coordinated site (nominally Mg²⁺). Despite a number of studies [Andrault, et al., 1998; Kesson, et al., 1995; Zhang and Weidner, 1999], the proportions of the two site types in the structure that are occupied by Al³⁺ are not well-constrained by experiment, limiting the possibilities for theoretical understanding of the properties of the phase. Atomistic computer simulations [Richmond and Brodholt, 1998] predicted that at high pressures, the charge-coupled substitution of two Al for one Si plus one Mg cation should be energetically favored in the iron-free system; more accurate density functional theory calculations suggested a changeover from an oxygen vacancy mechanism to stoichiometric coupled substitution at about 30 GPa at 0 K, and at perhaps 50 to 60 GPa at mantle temperatures [Brodholt, 2000]. ²⁷Al NMR is an ideal tool for resolving this problem, particularly with the recent development of technology that allows high-resolution spectra to be collected on very small (1 to 3 mg) high-pressure samples, including magnetic field strengths up to 18.8 Tesla. Here we describe a study that suggests that the coupled substitution of Al into the perovskite octahedral sites and into distorted modifications of the large, central site in the structure is the primary mechanism of solid solution even at pressures equivalent to the top of the lower mantle.

High-pressure phase equilibrium studies indicate that most or all of the Al₂O₃ in the lower mantle (about 3 to 5% by weight [Anderson, 1989; Wood and Rubie, 1996]) can in fact be accommodated by MgSiO₃ perovskite [Irfune, 1994; Kesson, et al., 1995]. The trivalent cation has significant effects on the physical

properties of the phase, which need to be understood before fully accurate interpretations of the mantle's seismic velocity, density structure, and electrical conductivity, and thus its mineralogy, composition, and convective regime can be made [Dobson and Brodholt, 2000; Brodholt, 2000; Weidner and Wang, 1998; Zhang and Weidner, 1999]. In addition, the transition from lower-pressure mantle phases to the perovskite structure, and the partitioning of Fe between MgSiO₃ perovskite and other phases, is strongly affected by the energetics of the Al solid solution [McCammon, 1997; Wood and Rubie, 1996].

A recent Al XAFS study [Andrault, et al., 1998] appeared to be consistent with a coupled substitution mechanism (⁶Si + ⁸Mg = ⁶Al + ⁸Al, where [n] indicates coordination number) in which Al³⁺ is partitioned equally between the two site types and local charge balance is maintained. However, this interpretation of the data was not completely unique, in part due to the absence of ¹⁸Al model phases. Bond valence arguments [Kudoh, et al., 1992] suggest that the nominally eight-coordinated site should be too large for Al³⁺. Other solution mechanisms have been proposed, such as the occupation by Al³⁺ of only octahedral sites, accompanied by some type of vacancy or other defect to maintain charge balance: oxygen vacancies are known, for example, to be common in low pressure perovskite-structured oxides [Navrotsky, 1999; Smyth, 1989]. These mechanisms were explored by recent calculations [Brodholt, 2000; Richmond and Brodholt, 1998], which also emphasized the likely importance of Al³⁺/Fe³⁺ coupling in natural mantle perovskites.

Application of ²⁷Al NMR to this problem has been inhibited by the small size of available samples (generally less than about 3 mg per synthesis run, compared to 100 to 300 mg for typical solid-state NMR experiments), and by the broadening effects of second-order quadrupolar coupling. The latter reduces the spectral resolution for this nuclide (nuclear spin = 5/2), and can make interpretations of spectra non-unique. These problems can be largely overcome by use of solid-state NMR probes with small inherent sample volumes and thus high sensitivity, and by collection of spectra at as high external magnetic fields as possible. ²⁹Si NMR is a useful complement to more fully characterize such materials. There are no direct effects of quadrupolar coupling on this spin = 1/2 nuclide, but its low natural abundance necessitates isotopic enrichment for NMR studies of very small samples in which peaks are broadened by disorder, as in glasses and disordered crystals.

Experimental Methods, Sample Synthesis and Characterization

Samples were synthesized from a glass of nominal composition 10.0 mol % Al₂O₃ and 90.0 mol % MgSiO₃, produced by

Copyright 2001 by the American Geophysical Union.

Paper number 2000GL012279.
0094-8276/01/2000GL012279\$05.00

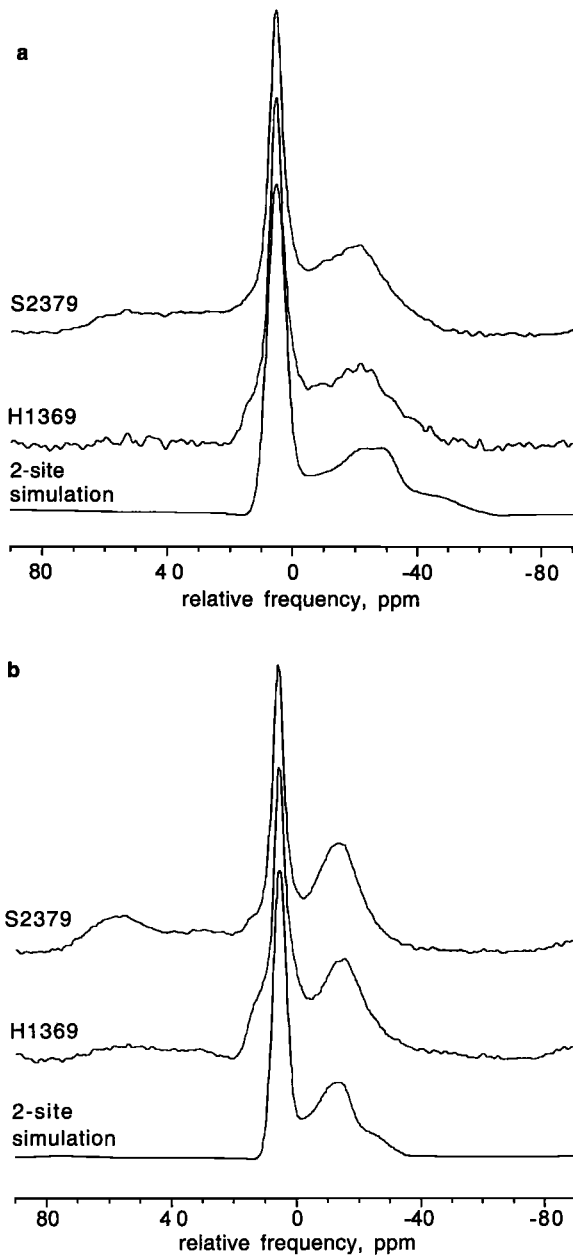


Figure 1. ^{27}Al magic-angle spinning (MAS) spectra of Al-containing MgSiO_3 perovskites, collected at (a) 14.1 Tesla and (b) 18.8 T. The minor shoulder at about 15 ppm may be an artifact of background subtraction. Spinning sidebands cause slight upturn in baselines at ends of plotted spectra. Intensities (arbitrary units) are scaled to same maximum height here and in Figure 2. Approximate simulation is described in text.

standard melt-quench techniques at 1640 °C but using 95% isotopically enriched $^{29}\text{SiO}_2$. To speed spin-lattice relaxation, 0.1 wt % cobalt oxide was added, a concentration too small to affect structural results. High pressure syntheses were carried out in a multi-anvil apparatus with 1200 ton press at the Bayerisches Geoinstitut, using Re capsules and a "7/3" high pressure cell assembly [Rubie, 1999]. At 26–28 GPa, sample H1369 was run at 1450 ± 50 °C and sample S2379 at 1750 °C. Electron microprobe data gave the molar Mg/Si ratio of 1.01 ± 0.02 , with a close-to-nominal 10.1 ± 0.2 wt % Al_2O_3 . Powder x-ray diffraction with Rietveld analysis showed the presence of perovskite, about 3 mol % stishovite, and no other phases.

NMR spectra were collected with Varian Inova 600 and Inova 800 spectrometers, using Varian/Chemagnetics probes with 3.2 mm rotors spinning at 18 to 20 kHz. Single pulse acquisition was used, with short ($0.3 \mu\text{s}$, 30° rf tip angle for the solid) pulses and delay times chosen to optimize signal to noise and ensure quantitative excitation. Pulse delays of 0.05 to 0.2 s for ^{27}Al and 1 to 60 s for ^{29}Si were used, with no significant differential relaxation. Frequencies (156.3 and 119.1 MHz for ^{27}Al and ^{29}Si at 14.1 Tesla, 208.4 for ^{27}Al at 18.8 T) were referenced to external samples of aqueous $\text{Al}(\text{NO}_3)_3$ and tetramethyl silane. Data were processed with a minimum of Gaussian apodization, chosen to produce no noticeable peak broadening. A minor background signal for ^{27}Al was subtracted. Sample masses ranged from 1.0 (H1369) to 3.3 mg (S2379). Spectra contained no detectable signature of stishovite in the spectra, which would produce a narrow peak at 191.3 ppm if it was pure SiO_2 [Xue and Stebbins, 1993]; no evidence for a garnet phase is present, which would be clearly detectable in both ^{29}Si and ^{27}Al spectra (Stebbins et al., unpublished data) [McMillan, et al., 1989; Phillips, et al., 1992].

Results and Discussion

In the ^{27}Al MAS NMR spectra (Fig. 1), the most prominent feature, a narrow (4.5 ppm width at half-height) peak with an isotropic chemical shift $\delta_{\text{iso}} = 5.8 \pm 0.2$ ppm, is the signature of Al in a symmetrical, six-coordinated site. The high symmetry, strongly suggesting six ^{6}Si neighbors (and hence few or no $^{6}\text{Al-O-}^{6}\text{Al}$ pairs), is confirmed by the unusually small quadrupolar coupling constant (C_Q) for the peak, estimated at about 1 MHz from data collected at multiple magnetic fields. In some samples, a smaller, broad feature at higher frequency (centered at 50 to 60 ppm) indicates a minor amount of ^{4}Al , probably in a residual glassy phase left uncrystallized in the cooler ends of the high pressure sample capsule. The presence of glass is confirmed by a broad ^{4}Si peak centered at about -82 ppm in the ^{29}Si spectra (Fig. 2), whose width and shape are consistent only with glass. For both nuclides, these features vary considerably (and together) in relative intensity from sample to sample, and thus are probably not

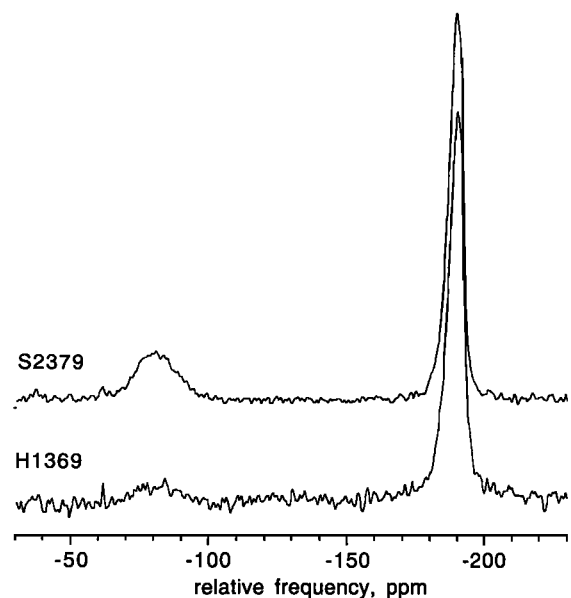


Figure 2. ^{29}Si MAS NMR spectra of Al-containing MgSiO_3 perovskites, collected at 14.1 T. Spinning sidebands are outside of the frequency range plotted.

inherent to the crystalline perovskite. The NMR peak shapes for ^{29}Si and ^{27}Al in the lower frequency regions are not significantly changed by the varying amounts of these ^{41}Si or ^{41}Al signals, again suggesting that the latter are not components of the perovskite phase.

Also in the ^{27}Al spectra, a second, larger, broad peak occurs at lower frequency (maximum at about -21 ppm in the 14.1 T data). The fact that this peak (unlike the narrow peak) changes width and position significantly with magnetic field demonstrates that a major contribution to both comes from the second order quadrupolar coupling, which broadens the peak and shifts its center of gravity to a frequency lower (to the right in plots) than the true chemical shift. The roughly triangular shape of this feature indicates a range in NMR parameters resulting from a range in local structure (bond distances, angles, etc.) probably linked to cation disorder. The peak shape cannot be accurately simulated without arbitrary assumptions about the nature of this disorder and its detailed effects on spectral parameters. However, an approximation of this peak shape with a single set of parameters, chosen to give the best fit at both fields, does serve to estimate its relative intensity, and to assess at least rough means of the quadrupolar coupling and the chemical shift, as has commonly been done for spectra of glasses [Schmidt *et al.*, 2000]. The resulting parameters, which generate the simulated peaks in Figure 1 when convolved with significant Gaussian broadening, are $\delta_{\text{iso}} = 4$ ppm, $C_Q = 10$ MHz, and a quadrupolar asymmetry parameter $\eta_Q = 0.7$. Comparing the two samples with different glass contents, the similarity of the peak shapes for the perovskite phase (e.g. -50 to 10 ppm in the 14.1 T data), including the relative areas of the two main components, demonstrates a lack of differential compositional partitioning between the glassy and crystalline phases.

The simulations shown in Figure 1 were calculated using an assumption of a 1:1 area ratio of the two peaks, not with fitted intensities. The matches to the experimental data at both fields are relatively good, given some perturbation of ^{61}Al peak heights by the low frequency "tails" of the signal from the glassy phase and some imperfection in the background subtraction procedure necessitated by the small sample sizes. This result indicates that a 1:1 coupled substitution of Al in MgSiO_3 is the major solution mechanism, as no other obvious arrangement of Al in the structure would give rise to an equal distribution in two distinct types of sites.

The ^{27}Al NMR data also seem to rule out a predominant mechanism in which oxygen vacancies provide charge compensation for substitution of Al^{3+} for Si^{4+} . For example, such a vacancy adjacent to an octahedral Al^{3+} cation should convert it to an ^{51}Al site with some degree of distortion depending on the extent of local structural relaxation. Particularly in the data for the sample with the smallest glassy component (H1369), there is no evidence for significant concentrations of such sites, which should have δ_{iso} in the range of about 30 to 45 ppm. At the extremely high field used here (18.8 T), peaks for even highly distorted sites with C_Q as high as any described in aluminosilicates (>15 MHz) should be readily detectable. Similarly, the ^{29}Si spectra (Fig. 2) show no evidence for ^{51}Si sites, expected near to -150 ppm [Stebbins and Poe, 1999]. The lack of any ^{29}Si NMR peaks at higher chemical shifts than that for normal ^{61}Si indicates as well the absence of sites with unusually long Si-O distances or higher coordination, as suggested by some alternate models for Al substitution in which some Si occupies the larger Mg site [Richmond and Brodholt, 1998].

In some low-pressure, perovskite-structured oxides with large contents of O vacancies, e.g. brownmillerite

($\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$), ordering leads to tetrahedral cations [Brodholt, 2000]. It is possible that signal from a relatively small concentration of such sites in our samples could be hidden by the signal from the glassy component. The presence of a few % stishovite also suggests the possibility of some Si deficiency in our perovskite samples, where, by stoichiometry alone, as much as 15 to 20% of the Al could be associated with O vacancies. Stishovite was not detected in the ^{29}Si spectra, suggesting that significant Al solid solution in this phase could have broadened its peak to the extent of being indistinguishable from the perovskite peak. Such variation from stoichiometry of the stishovite would reduce this estimate of the vacancy-compensated Al in the perovskite phase even further.

We thus conclude that among the list of 10 mechanisms for Al substitution in mantle perovskite listed recently [Richmond and Brodholt, 1998], the one that predominates in our samples is that in which one Mg and one Si are each replaced by one Al cation. In recent theoretical work, a transition to this mechanism from an oxygen vacancy mechanism was predicted at pressures above about 30 GPa at 0 K, not much higher than the run pressures for our samples [Brodholt, 2000]. However, the correction to experimental (and mantle) temperatures is not well constrained without detailed knowledge of the effects of disorder of both vacancies and cations on configurational and vibrational entropy. Some role for vacancies in relatively low P, Al-doped perovskites does appear to be consistent with the correlation of observed and calculated bulk moduli and suggestions of Si deficiency [Brodholt, 2000]. Given the possibility of some "mixing" of solid solution mechanisms in our samples, it is likely that variations in experimental P and T conditions, as well as Al content, could significantly affect the vacancy content and ordering state. Such variables should be investigated in future studies.

Our results may also indicate a complication of the simplified view of Al^{3+} substitution into perovskite taken in most previous discussions. The chemical shift derived for the broad peak (Al in the Mg site) from our "two site" approximation is consistent with six-coordination: ^{61}Al sites in silicates typically have δ_{iso} of 0 to 16 ppm [Stebbins, 1995]. It is possible that the "large", normally eight-coordinated site in MgSiO_3 perovskite partially collapses around the "too-small" Al^{3+} cation, at least at ambient P and T. For example, even in the pure Mg phase, two of the eight Mg-O distances are unusually long [Horiuchi, *et al.*, 1987]. However, our estimate of δ_{iso} of about 4 ppm is more likely to be the upper bound of a range of δ_{iso} in a phase with considerable cation disorder, suggesting that a significant fraction of the Al sites could indeed have smaller values for both C_Q and δ_{iso} . The latter would be consistent with coordination numbers higher than six.

Further information about structural disorder is apparent in the ^{29}Si spectra (Fig. 2). The ^{61}Si NMR peak for Al-substituted MgSiO_3 perovskite is much broader (6 ppm width at half height) than is typical for Al-free silicates (<0.5 ppm) [Kirkpatrick, *et al.*, 1991; Stebbins and Poe, 1999]. Its maximum is shifted up in frequency from the -191.7 ppm of Al-free perovskite [Kirkpatrick, *et al.*, 1991] to -189.2 ppm, and it is asymmetrical towards higher frequency, all likely consequences of a range in the number of ^{61}Al neighbors. Al-Mg disorder may also broaden the ^{61}Si peak. It is clear that disorder among both octahedral Al and Si, perhaps with a modified "aluminum avoidance" that limits the number of $^{61}\text{Al-O}^{61}\text{Al}$ pairs, as well as among Al and Mg in the larger site, will need to be considered in thermodynamic models of the phase, although it is possible that disorder will be reduced by correlation of Al on adjacent octahedral and "large" sites to maintain local charge balance.

New NMR technology has opened up a wealth of new options for the resolution of complex structural questions in even single experimental runs from the highest pressures obtainable in "multi-anvil" apparatus: useful ^{27}Al and ^{29}Si spectra can now be obtained even without isotopic enrichment for the latter nuclide [Stebbins and Poe, 1999]. For the purposes of understanding the solid solutions of MgSiO_3 perovskite in compositions most common in nature, the work described here may be even more useful in refining the interpretation of Al x-ray absorption spectra [Andraut, et al., 1998], as the latter technique can be applied to the Fe+Al bearing systems so important in the earth's lower mantle. The proposed coupled substitution of Al^{3+} and Fe^{3+} [Richmond and Brodholt, 1998; Wood and Rubie, 1996], perhaps of major importance in natural phase equilibria, can thus be further investigated.

Acknowledgments. We thank David Rice (Varian Inc.) for assistance in collection of the NMR data at 18.8 T, Professor Joseph Puglisi for access to this instrument in the Stanford Magnetic Resonance Laboratory, Bob Jones for the electron microprobe analyses, Brent Poe for help with the high-pressure experiments, and Brian Phillips and several anonymous reviewers for helpful comments. This work was supported by the U.S. NSF (J.F. Stebbins), by the EU-TMR large scale facilities program (D.C. Rubie, Bayerisches Geoinstitut) and by an NSERC (Canada) postdoctoral fellowship to S. Kroeker.

References

- Andraut, D., D. R. Neuville, A. M. Flank, and Y. Wang, Cation sites in Al-rich MgSiO_3 perovskites, *Am. Mineral.*, **83**, 1045-1053, 1998.
- Brodholt, J.P. Pressure-induced changes in the compression mechanism of aluminous perovskite in the Earth's mantle, *Nature*, **407**, 620-622, 2000.
- Dobson, D. P., and J. P. Brodholt, The electrical conductivity and thermal profile of the earth's mid-mantle, *Geophys. Res. Lett.*, **27**, 2325-2328, 2000.
- Horiuchi, H., E. Ito, and D. J. Weidner, Perovskite-type MgSiO_3 : Single-crystal X-ray diffraction study, *Am. Mineral.*, **72**, 357-360, 1987.
- Irifune, T., Absence of an aluminous phase in the upper part of the Earth's lower mantle, *Nature*, **370**, 131-133, 1994.
- Kesson, S. E., J. D. FitzGerald, J. M. G. Shelley, and R. L. Withers, Phase relations, structure and crystal chemistry of some aluminous silicate perovskites, *Ear. Planet. Sci. Lett.*, **134**, 187-201, 1995.
- Kirkpatrick, R. J., D. Howell, B. L. Phillips, X. D. Cong, E. Ito, and A. Navrotsky, MAS NMR spectroscopic study of $\text{Mg}^{29}\text{SiO}_3$ with perovskite structure, *Am. Mineral.*, **76**, 673-676, 1991.
- Knittle, E., and R. Jeanloz, Synthesis and equation of state of $(\text{Mg,Fe})\text{SiO}_3$ perovskite to over 100 GPa, *Science*, **235**, 669-670, 1987.
- Kudoh, Y., C. T. Prewitt, L. W. Finger, and E. Ito, Ionic radius-bond strength systematics, ionic compressibilities, and an application to $(\text{Mg,Fe})\text{SiO}_3$ perovskites, in *High-Pressure Research: Application to Earth and Planetary Sciences*, edited by Y. Syono and M. H. Manghiani, pp. 215-218, American Geophysical Union, Washington, D.C., 1992.
- McCammon, C., Perovskite as a possible sink for ferric iron in the lower mantle, *Nature*, **387**, 694-696, 1997.
- McMillan, P., M. Akaogi, E. Ohtani, Q. Williams, R. Nieman, and R. Sato, Cation disorder in garnets along the $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} - \text{Mg}_4\text{Si}_4\text{O}_{12}$ join: an infrared, Raman, and NMR study, *Phys. Chem. Minerals*, **16**, 428-435, 1989.
- Navrotsky, A., A lesson from ceramics, *Science*, **284**, 1788-1789, 1999.
- Phillips, B. L., D. A. Howell, R. J. Kirkpatrick, and T. Gasparik, Investigation of cation order in MgSiO_3 -rich garnet using ^{29}Si and ^{27}Al MAS NMR spectroscopy, *Am. Mineral.*, **77**, 704-712, 1992.
- Richmond, N. C., and J. P. Brodholt, Calculated role of aluminum in the incorporation of ferric iron into magnesium silicate perovskite, *Am. Mineral.*, **83**, 947-951, 1998.
- Rubie, D. C., Characterising the sample environment in multianvil high-pressure experiments, *Phase Trans.*, **68**, 431-451, 1999.
- Schmidt, B. C., T. Riemer, S. C. Kohn, H. Behrens, and R. Dupree, Different water solubility mechanisms in hydrous glasses along the Qz-Ab join: evidence from NMR spectroscopy, *Geochim. Cosmochim. Acta*, **64**, 513-526, 2000.
- Smyth, D. M., Defect equilibria in perovskite oxides, in *Perovskite: A structure of great interest to geophysics and materials science*, edited by A. Navrotsky and D. J. Weidner, pp. 99-104, American Geophysical Union, Washington, D.C., 1989.
- Stebbins, J. F., Nuclear magnetic resonance spectroscopy of silicates and oxides in geochemistry and geophysics, in *Handbook of Physical Constants*, edited by T. J. Ahrens, pp. 303-332, American Geophysical Union, Washington D.C., 1995.
- Stebbins, J. F., and B. T. Poe, Pentacoordinate silicon in high-pressure crystalline and glassy phases of calcium disilicate (CaSi_2O_5), *Geophys. Res. Lett.*, **26**, 2521-2523, 1999.
- Weidner, D. J., and Y. Wang, Chemical- and Clapeyron-induced buoyancy at the 660 km discontinuity, *J. Geophys. Res.*, **103**, 7431-7441, 1998.
- Wood, B. J., and D. C. Rubie, The effect of alumina on phase transformations at the 660-kilometer discontinuity from Fe-Mg partitioning experiments, *Science*, **273**, 1522-1524, 1996.
- Xue, X., and J. F. Stebbins, A ^{29}Si MAS NMR study of sub-Tg amorphization of stishovite at ambient pressure, *Phys. Chem. Minerals*, **19**, 480-485, 1993.
- Zhang, J., and D. J. Weidner, Thermal equation of state of aluminum-enriched silicate perovskite, *Science*, **284**, 782-784, 1999.

J. F. Stebbins, S. Kroeker, Dept. of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305-2115
(e-mail: stebbins@pangea.stanford.edu)

D. Andraut, Laboratoire des Géomatériaux, IPGP, 4 Place Jussieu, Paris 75252 France
(e-mail: andraut@ipgp.jussieu.fr)

(Received 08/31/00; revised 11/16/00;
accepted 11/29/00)